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(54) Title: SILICAS (57) Abstract An amorphous silica has a pore size distribution wherein 90 % of the pores have a diameter above 15 nanometers, and less than 20 % of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the amorphous silica having a CTAB surface area of less than 100 m ² /g, the amorphous silica having a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5 % by weight. It can be prepared by a precipitation route. It is used in thixotropic paints and lacquers.		

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SilicasTechnical field of the invention

5 The invention relates to silicas, a process for manufacturing these silicas and the use of these silicas as matting agents in thixotropic paints, varnishes and lacquers.

10 Background of the invention

Silica gels, usually referred to as xerogels in the dried form, are versatile materials for industrial purposes and find uses, particularly in the milled and/or micronised
15 state in which controlled particle size distributions can be produced, as a matting agent in paint and lacquer systems.

It is common for paints and varnishes to be structured by
20 the incorporation of a thixotropic medium. Such paints and varnishes can have the advantages of being dripless, easy to apply, prevent pigment settlement and can be put on vertical surfaces at high film thickness without sagging.

25 Resins prepared from alkyds and polyamides are frequently used as the main binder component in thixotropic alkyd coatings and thixotropic alkyd resins are commercially manufactured by, for example, Cray Valley Products under the name of Gelkyds.

30 The degree of thixotropy present in a paint or varnish can be controlled by the level of thixotropic alkyds utilised. They can be incorporated on their own or in combination with a conventional liquid resin to give complete
35 formulation flexibility. The range of the resultant paints and varnishes can therefore span from highly structured

(dripless) to only lightly structured (gel or viscous liquid).

5 It is often desirable to produce thixotropic paints or varnishes in matt, semi-matt or eggshell finishes, by the incorporation of a suitable silica. Unfortunately, this causes partial or total loss of the thixotropy depending upon the type of silica which is used.

10 Some silicas, such as Gasil 200 (obtainable from Joseph Crosfield & Sons) prove to have no significant negative effects on thixotropy but, in other respects they are not suitable as matting agents. In contrast, silicas based upon gel technology such as HP200 series products
15 (obtainable from Joseph Crosfield & Sons) prove to be good matting agents but adversely affect the thixotropy.

Up to now two solutions have been proposed which can be summarised as follows.

20 As a first solution, the matting agent is a standard silica and the thixotropic system is formulated to minimize negative interactions. Thixotropic alkyds manufacturers have used this solution by eliminating the random nature of the hydrogen bonding present in
25 conventional thixotropic alkyd resins and produced so-called Super-Gelkyds which are tolerant to polar groups. However such products have drawbacks in terms of delivery and handling since they have non melting characteristics
30 and cannot be supplied in mobile form in tankers. These products can also be sensitive to high shear rates.

As a second solution, instead of reformulating the thixotropic system, the matting agent is modified in order
35 to minimize its interactions with the thixotropic system. EP-A-442325 (Grace GmbH) describes a silica flattening agent

which is purported to be used in thixotropic polyamide-modified alkyd resins with no negative effect on their thixotropic behaviour. This is allegedly achieved by adding 1 to 25% by weight of a polyol to a silica. This
5 solution therefore requires an additional processing step.

Thus, there is a need for a silica which exhibits good matting properties whilst not adversely affecting the thixotropic nature of the thixotropic system to which it
10 is added.

It is therefore a first goal of the present invention to provide a silica with good matting properties that does not adversely affect the thixotropic behaviour of
15 thixotropic paints and lacquers based on polyamide-modified alkyd resins.

It is a second goal of the present invention to provide a process for manufacturing such silica.
20

It is a third goal of the present invention to provide thixotropic paints and lacquers based on polyamide-modified alkyd resins with a silica matting agent.

25 It has now been found that a silica with a specific pore size distribution and with a specific matting efficiency can be used as a matting agent in thixotropic paints and lacquers based on polyamide-modified alkyd resins without adversely affecting the thixotropic behaviour of the
30 system.

Summary of the invention

35 It is a first object of the present invention to provide an amorphous silica having a pore size distribution wherein 90% of the pores have a diameter above 15

nanometers, and less than 20% of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the amorphous silica having a CTAB surface area of less than 100 m²/g, the amorphous silica having a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5% by weight in a thixotropic modified alkyd paint system.

It is a second object of the present invention to provide a process for manufacturing an amorphous silica wherein, in a first step, sulphuric acid is added to, or mixed with, a sodium silicate solution having a SiO₂:Na₂O ratio of between 3.1 and 3.4 to form a slurry, after this first step the degree of neutralisation being between 50% and 88% and the SiO₂ concentration being between 6.5% and 7.5% by weight, the temperature of the slurry being maintained below 100°C and above 85°C, sulphuric acid being afterwards added to reach a pH of about 4, the resulting silica being then washed and dried.

It is a third object of the present invention to provide thixotropic paints and lacquers based on polyamide-modified alkyd resins, with a silica matting agent wherein the silica matting agent is an amorphous silica having a pore size distribution wherein 90% of the pores have a diameter above 15 nanometers, and less than 20% of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the amorphous silica having a CTAB surface area of less than 100 m²/g, the amorphous silica having a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5% by weight in a thixotropic modified alkyd paint system.

Definitions and test procedures

i. Nitrogen surface area - pore volume

5 Nitrogen surface area is determined by standard
nitrogen adsorption methods of Brunauer, Emmett and
Teller (BET) using a multi point method with an ASAP
2400 apparatus supplied by Micromeritics of the
U.S.A.. The samples are outgassed under vacuum at
10 270°C for at least one hour before measurement.
Surface area is calculated from the volume of
nitrogen gas adsorbed at p/p_0 0.98. This apparatus
also provides the pore size distribution from which
it is possible to get the pore size (D_{10}) for which
15 10% of the pores are below this pore size. In the
same manner, it is possible to get the pore size for
which 50% (D_{50}) and 90% (D_{90}) of the pores are below
this pore size. Additionally the pore volume (cm^3/g)
for a given range of pore size can be obtained from
20 the desorption curve.

ii. Matting efficiency

25 The matting efficiency of a silica flatting agent is
determined by dispersing the silica in a polyamide-
modified alkyd resin, drawing a film on a glass
plate, and allowing to air dry at room temperature in
a dust free atmosphere. The plates are then measured
for matting efficiency at 60° and 85° incidence angle
30 using a BYK multi glossmeter.

Formulation of thixotropic resin

	Parts by weight
Rutile Titania	28.4
Synolac 60W (*)	22.1
Gelkyd 320W (*)	39.0
White spirit	9.3
10% Calcium carboxylate	0.7
12% Cobalt octoate	0.2
24% Zirconium carboxylate	0.2
Methyl ethyl ketoxime	0.9

(*) Synolac 60W and Gelkyd 320W can be obtained from Cray Valley Products.

This formulation, in the absence of silica matting agent, gave gloss readings of 82 and 92 at angles of incidence of 60° and 85° respectively. The viscosity of this formulation was 20,768 mPa.s at 24 sec⁻¹ and 25°C.

The test resin contains a weight percent (3% or 5%) of the silica matting agent as defined in each example.

Into an 8 oz (250 cm³) glass jar weigh 47.5 g of thixotropic resin (formulation above). Using a glass rod stir into the paint an appropriate weight of silica until the powder completely wets out.

Following complete wetting stir the system at 1500 rpm for two minutes using a Heidolph stirrer (fitted with a Cowles type head). Draw a film onto a black glass plate (12" x 4") using a 100 µm block applicator and allow to air dry at room temperature, in a dust free atmosphere, over a period of 24 hours.

Assess the matting efficiency (expressed in gloss units) by reading at 60° and 85° incidence angle using a BYK multi glossmeter.

5 iii. Degree of neutralisation (DofN)

10 Knowing the quantity of sodium silicate which is to be neutralised it is possible to calculate the quantity of acid which is needed to complete the neutralisation. The degree of neutralisation must be understood as being the percentage of the required amount of acid which has been introduced at the end of the first acid addition.

15 iv. Thixotropy - viscosity

20 The viscosity of a thixotropic resin, and a silica flatted thixotropic resin, is determined after pre conditionning of the system at 55-60°C , to provide a consistent shear history for the systems. The pre conditioned samples are then allowed to stand for 24 hours at 25°C and are measured at 25°C using a Haake viscometer fitted with a 1° cone and plate.

25 The formulation of polyamide modified thixotropic alkyd resin is summarised in section (ii) (Matting efficiency).

30 The flatted resin contains 5% by weight of silica with respect to the weight of the thixotropic formulation.

35 Into a 60 cm³ screw cap jar weigh 47.5 g of the thixotropic resin. Heat the resin to 55-60°C and using a glass rod stir in 2.5 g of silica flatting agent until the powder is fully wetted.

5 Store the flattened system at 25°C for 24 hours, after which the viscosity can be determined using a Haake viscometer. The viscometer (Haake RV 12) is fitted with a PK 100 sensor system, an M 150 measuring head and a PK 1, 1° cone.

10 A flow curve is determined (at 25°C) one minute after loading the sample by applying an increasing shear rate, from 0 to 324 sec⁻¹, over a two minute period. The viscosity is calculated at 24 sec⁻¹ from this increasing rate curve.

15 The viscosity of the formulation in the absence of silica matting agent was 20,768 mPa.s

v. Weight mean particle size

20 The weight mean particle size is determined with the aid of a Malvern Mastersizer using 45 mm path length lens. This instrument, made by Malvern Instruments, Worcestershire uses the principle of Fraunhofer diffraction utilising a low power He/Ne laser. Before measurement the sample was dispersed ultrasonically in water for a period of 7 minutes to form an aqueous suspension. The Malvern Mastersizer measures the weight particle size distribution of the silica. The weight mean particle size (d_{50}), the 10 percentile (d_{10}) and the 90 percentile (d_{90}) are easily obtained from the data generated by the instrument.

30

vi. CTAB surface area

35 This method determines the specific surface area of samples, exclusive of area contained in micropores too small to admit hexadecyltrimethyl ammonium

bromide (cetyltrimethyl ammonium bromide, commonly referred to as CTAB) molecules.

5 The isotherm for adsorption of an aqueous solution of CTAB at a charged surface has a long horizontal plateau corresponding to a bilayer coverage of the substrate surface. Rapid equilibration is achieved by using mechanical agitation. Titration with sodium dodecyl sulphate solution is used to determine the
10 unadsorbed CTAB after removal of the dispersed silica by centrifugation.

Into a 50 cm³ screw-cap jar weight between 0.10 and 0.25 g of silica, depending upon surface area to be
15 determined. For high surface areas, which lead to low CTAB titrations, the lower weight is employed. Add 25 cm³ of 0.01 mol.dm⁻³ CTAB solution and bring the pH of the mixture to 9.0 with 0.1 mol.dm⁻³ NaOH solution. Stopper the jar and agitate for 1 hour in a water
20 bath set at 25°C. Settle the suspension centrifugally and transfer 5 cm³ of the supernatant into a 50 cm³ measuring cylinder. Add 10 cm³ of deionised water, 15 cm³ of chloroform, 10 cm³ of mixed indicator solution (dimidium bromide/disulphine blue obtainable from BDH
25 Ltd, Poole, Dorset, England) and titrate with 0.005 mol.dm⁻³ sodium dodecyl sulphate solution, previously calibrated by a standard CTAB solution. The titration end point is that point at which the chloroform layer becomes pale-pink. Record the volume of sodium
30 dodecyl sulphate to reach the end point as V₂ cm³. Conduct a blank titration in a similar manner on 5 cm³ of the stock CTAB solution and record the volume of sodium dodecyl sulphate as V₁ cm³.

Calculate the CTAB surface per gram of silica by the following equation in which the calculation is based on a molecular cross section of the bromide of 35 Å²:

$$5 \quad \text{CTAB surface area} = \frac{(V_1 - V_2) \times 5.27}{W} \times (0.5)$$

Where W = Weight of silica samle (in grams)
0.5 accounts for bi-layer formation.

10

Specific description of the invention

The invention is further illustrated but not limited by the following examples wherein percentages are in weight unless otherwise specified.

Example 1

20 A heated stirred reaction vessel was used for the
silicate/acid reacton.

Mixing is an important feature in the reaction of silicate and sulphuric acid. Consequently fixed specifications as listed in Chemineer Inc. Chem Eng. April 26th 1976 pages 102-110 have been used to design the baffled heated stirred reaction vessel. Whilst the turbine design is optional to the mixing geometry, a 6-bladed 30° pitched bladed unit has been chosen for the experiments in order to ensure maximum mixing effectiveness with minimum shear.

30

The solutions used in this Example were as follows:

i) Sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.29:1 and a SiO_2 content of 17.2% by weight.

35

ii) A sulphuric acid solution of specific gravity of 1.12.

No electrolyte solution was added.

13.6 litres of water was placed in the vessel together with 0.12 litres of sodium silicate solution. This mixture
5 was then stirred and heated to 98°C.

11.4 litres of sodium silicate and 4.8 litres of sulphuric acid were then added simultaneously over a period of 20 minutes with stirring whilst maintaining the temperature
10 at 98°C. The flow rates of the silicate and acid solutions were uniform throughout the addition period to ensure that a constant pH of 10 was maintained in the vessel.

Silicate slurry was then aged at pH 10 for 50 minutes at
15 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

20 The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

Example 2

25 The same reaction vessel, with the same stirrer, was used as in Example 1.

The solutions used in this Example were as follows:

30 i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.29:1 and a SiO₂ content of 16.75% by weight.

ii) A sulphuric acid solution of specific gravity of 1.13.

35 iii) 3.8 litres of a 25% (w/w) sodium chloride solution.

13.6 litres of water was placed in the vessel together with 11.3 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

5 4.89 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period. The final pH after the acid addition was 9.

10

3.8 litres of a 25% (w/w) sodium chloride solution was then added over 18 minutes, the temperature being maintained at 98°C.

15

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

20

Example 3

The same reaction vessel, with the same stirrer, was used as in Example 1.

25

The solutions used in this Example were as follows:

i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.29:1 and a SiO₂ content of 17.2% by weight.

30

ii) A sulphuric acid solution of specific gravity of 1.12.

13.6 litres of water was placed in the vessel together with 11.5 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

35

4.84 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period. The
5 final pH after the acid addition was 11.

The slurry was then aged over a period of 20 minutes at a temperature of 98°C.

10 Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.
15

Example 4

A larger reaction vessel than the one used in Example 1 but with the same configuration of the vessel geometry, baffles and stirrer was used.
20

The solutions used in this Example were as follows:

i) Sodium silicate solution having a SiO₂:Na₂O ratio of
25 3.28:1 and a SiO₂ content of 16.62% by weight.

ii) A sulphuric acid solution of specific gravity of 1.12.

iii) 40 litres of a 25% (w/w) sodium chloride solution.
30

83.5 litres of water was placed in the vessel together with 80.2 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

35 27.96 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the

temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period.

5 40 litres of a 25% (w/w) sodium chloride solution was then added over 15 minutes, the temperature being maintained at 98°C.

10 Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

Example 5

15 The same reaction vessel, with the same stirrer, was used as in Example 1.

The solutions used in this Example were as follows:

- 20
- i) Sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.25:1 and a SiO_2 content of 17.1% by weight.
 - 25 ii) A sulphuric acid solution of specific gravity of 1.13.
 - iii) 4.0 litres of a 25% (w/w) sodium chloride solution.

13.35 litres of water was placed in the vessel together with 11.6 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

30

5.03 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period.

35

4.0 litres of a 25% (w/w) sodium chloride solution was then added over 18 minutes, the temperature being maintained at 98°C.

5 The slurry was then aged during 10 minutes at 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

10 The resultant slurry was then filtered and washed with water to remove excess electrolyte dried and micronised.

The physical properties of Examples 1 to 5 are summarised in the following Table 1 wherein:

- 15 - S.A. = Surface Area to nitrogen (m^2/g)
 - P.V. = Total Pore Volume to nitrogen (cm^3/g)
 (of pores with pore diameter between 1.7
 and 300 nm)
 - P.V.(10-30) = Pore Volume to nitrogen of pores
 20 having a diameter between 10 and
 30 nm. (cm^3/g)
 - $X = 100 \times \frac{\text{P.V.}(10-30)}{\text{P.V.}}$
 - Pore size distribution: D_{10} , D_{50} , D_{90} in nanometers as
 25 above defined in "Definitions and Test procedures"
 section i).
 - M.E. at 60° = Matting efficiency at 60° at 5%
 loading (in gloss units)
 - M.E. at 85° = Matting efficiency at 85° at 5%
 30 loading (in gloss units)
 - V. = viscosity (mPa.s)
 - d_{10} , d_{50} , d_{90} = percentiles of the particle size
 distribution (microns) after drying and
 micronization,
 35 - S = Surface Area to CTAB (m^2/g)
 - NM means that the parameter was not measured

Table 1

Example	1	2	3	4	5
S.A. (m ² /g)	177	209	215	230	NM
P.V. (cm ³ /g)	1.09	1.31	0.91	1.78	NM
P.V. (10-30) (cm ³ /g)	0.13	0.20	0.16	0.19	NM
X	11.9	15.4	17.6	10.7	NM
S (m ² /g)	55	82	77	74	70
D ₁₀ (nm)	22	21	16	28	NM
D ₅₀ (nm)	60	50	50	60	NM
D ₉₀ (nm)	>100	>100	>100	>100	NM
M.E. at 60°	15	6	6	11	7
M.E. at 85°	36	10	10	26	12
V. (mPa.s)	18638	18638	14910	20235	14378
d ₁₀ (μm)	2.6	3.7	4.0	3.0	4.1
d ₅₀ (μm)	5.8	7.4	7.6	6.9	7.1
d ₉₀ (μm)	12.8	14.9	14.3	14.6	20.3

Example 6

A number of preparations have been made, altering the temperature, the percentage SiO₂ of the sol after the first acid addition, the Degree of Neutralization, the NaCl:SiO₂ ratio and the ageing time in order to identify the key process variables controlling thixotropy and matting.

Preparations are based upon a sol volume of 30 litres, the sol consisting of water, sodium silicate and first acid addition. The method of addition being according to Example 2 or 5 depending on the presence of an ageing step of 10 minutes.

The results are summarised in the following Table 2 wherein.

- $\text{SiO}_2(\%)$ represents the SiO_2 concentration in percent by weight at the end of the first acid addition,
- DofN represents the Degree of Neutralization,
- $\text{NaCl}:\text{SiO}_2$ represents the weight ratio of NaCl and SiO_2 ,
- M.E. at 60° = Matting efficiency at 60° at 3% loading (in gloss units),
- M.E. at 85° = Matting efficiency at 85° at 3% loading (in gloss units),
- V. = viscosity (mPa.s)
- d_{10} , d_{50} , d_{90} = percentiles of the particle size distribution (microns) after drying and micronization.
- S = Surface Area to CTAB (m^2/g)
- NM means that the parameter was not measured,

Table 2

Sample	1	2	3	4	5	6
Temperature ($^\circ\text{C}$)	80	80	80	80	80	80
$\text{SiO}_2(\%)$	6.6	6.6	6.6	7.3	7.3	7.3
10 minutes Ageing	No	No	Yes	No	No	Yes
DofN (%)	70	84	70	70	84	70
$\text{NaCl}:\text{SiO}_2$	0.5:1	1:1	1:1	1:1	0.5:1	0.5:1
d_{10} (μm)	2.7	4.2	4.6	4.5	3.1	3.1
d_{50} (μm)	4.8	8.5	8.6	9.1	5.9	5.6
d_{90} (μm)	15.8	19.2	16.5	19.4	12.0	10.9
M.E. 60°	22	20	13	12	20	21
M.E. 80°	52	32	20	16	45	55
S (m^2/g)	NM	NM	150	116	134	NM
Viscosity (mPa.s)	7455	<3000	<3000	<3000	<3000	<3000

Table 2 (continued)

	Sample	7	8	9	10	11	12
5	Temperature (°C)	80	88	88	98	98	98
	SiO ₂ (%)	7.3	7.0	7.0	6.6	6.6	6.6
	10 minutes Ageing	Yes	No	No	No	Yes	Yes
	DofN (%)	84	84	84	70	70	84
10	NaCl:SiO ₂	1:1	0.5:1	1:1	1:1	0.5:1	1:1
	d ₁₀ (μm)	3.8	3.8	2.7	3.9	3.5	3.2
	d ₅₀ (μm)	8.0	8.0	4.8	9.7	9.6	6.6
	d ₉₀ (μm)	16.9	16.9	8.2	25.9	27.7	13.7
	M.E. 60°	18	22	19	23	37	15
15	M.E. 80°	36	55	56	46	64	42
	Viscosity (mPa.s)	<3000	18638	18105	17040	18638	12780

20	Sample	13	14	15	16	17	18
	Temperature (°C)	98	98	98	98	98	98
	SiO ₂ (%)	7.0	7.0	7.3	7.3	7.3	7.3
25	10 minutes Ageing	No	No	No	No	Yes	Yes
	DofN (%)	70	84	70	84	70	84
	NaCl:SiO ₂	1:1	0.5:1	0.5:1	1:1	1:1	0.5:1
	d ₁₀ (μm)	1.2	3.7	4.5	3.2	4.1	4.1
	d ₅₀ (μm)	5.3	7.4	11.0	6.0	9.5	7.1
30	d ₉₀ (μm)	11.9	14.9	27	10.6	21.0	20.3
	M.E. 60°	48	14	23	15	19	21
	M.E. 80°	81	30	31	38	26	37
35	Viscosity (mPa.s)	31950	18638	17040	14910	18105	14378

(*) - in the above table, the thixotropy of the preparation was completely destroyed in preparation 2, 3, 4, 5, 6, 7, and the viscosity was below 3000 mPa.s.

5 It can be seen that, none of the samples prepared at 80°C combine good retention of thixotropy with satisfactory matting efficiency.

10 In other respects the samples prepared at a temperature of 88 and 98°C combine a good retention of thixotropy with a satisfactory matting efficiency. It can be noticed from the above data that working at a temperature above 85°C the viscosity of the system is always maintained to a significant level even though, for highly thixotropic systems, a viscosity of 13,500 mPa.s is considered as the lower acceptable figure. That means that it is possible to produce a thixotropic paint or lacquer with a matting agent wherein the viscosity is reduced by less than 35% whereas the matting efficiency is less than 20 gloss units at an incidence angle of 60° and a loading of 5% by weight in a thixotropic modified alkyd paint system.

25 The percentage of SiO₂ after the first acid addition has to be below 7.5 and above 6.5% otherwise the matting efficiency as well as the thixotropy can be dramatically affected.

Comparative Example 1

30 An amorphous silica (Gasil 200 obtainable from Joseph Crosfield & Sons) with a small pore size distribution ($D_{10}=2.5$ nm, $D_{50}=2.8$ nm, $D_{90}=12.0$ nm) was tested as a matting agent in a thixotropic paint.

35 The particle size distribution was as follows:

20

- $d_{10} = 1.8 \mu\text{m}$
- $d_{50} = 4.2 \mu\text{m}$
- $d_{90} = 8.0 \mu\text{m}$

5 The matting efficiency as well as the influence on thixotropy were assessed according to the above described methods.

The results were as follows.

10 - Matting efficiency:

Angle	60	85
Loading		
3%	79	94
5%	74	93

15

- Viscosity: 15000 mPa.s

20 It is apparent that this silica has no significant detrimental effect on thixotropy but cannot be used as a matting agent because of its poor matting efficiency.

Comparative Example 2

25 Another amorphous silica (HP210 obtainable from Joseph Crosfield & Sons) with a wide pore size distribution ($D_{10}=12.0 \text{ nm}$, $D_{50}=19.0 \text{ nm}$, $D_{90}=27.0 \text{ nm}$) was also tested as in comparative Example 1.

30 The product is widely used as a matting silica and has the following particle size distribution:

- $d_{10} : 2.9 (\mu\text{m})$
- $d_{50} : 6.5 (\mu\text{m})$
- $d_{90} : 11.0 (\mu\text{m})$

35

The results were as follow.

21

- Matting efficiency:

Angle	60	85
Loading		
5%	8	21

5

- Viscosity: <3000 mPa.s (non thixotropic)

Although this silica gives a very good matting efficiency,
it totally destroys the thixotropy of the system.

10

Claims

1. Amorphous silica having a pore size distribution wherein 90% of the pores have a diameter above 15
5 nanometers, and less than 20% of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the amorphous silica having a CTAB surface area of less than 100 m²/g, the amorphous silica having a matting efficiency of below 20 gloss units at an incidence angle
10 of 60° and a loading of 5% by weight.
2. Process for manufacturing an amorphous silica wherein, in a first step, sulphuric acid is added to, or mixed with, a sodium silicate solution having a SiO₂:Na₂O
15 ratio of between 3.1 and 3.4 to form a slurry, after this first step the degree of neutralisation being between 50% and 88% and the SiO₂ concentration being between 6.5% and 7.5% by weight, the temperature of the slurry being maintained below 100°C and above 85°C, sulphuric acid
20 being afterwards added to reach a pH of about 4, the resulting silica being then washed and dried.
3. Process according to claim 2 wherein, after the first acid addition, sodium chloride is added to reach an
25 NaCl:SiO₂ ratio of 0.25:1 and 1:1.
4. Process according to claim 2 wherein, after the first acid addition the slurry is aged, at a temperature above 85°C, for a period of between 10 to 60 minutes.
30
5. Thixotropic paints and lacquers based on polyamide-modified alkyd resins, with a silica matting agent wherein the silica matting agent is an amorphous silica having a pore size distribution wherein 90% of the pores have a
35 diameter above 15 nanometers, and less than 20% of the pore volume is in pores having a pore diameter between 10

and 30 nanometers, the amorphous silica having a CTAB surface area of less than 100 m²/g, the amorphous silica having a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5% by weight.

5

6. Use of a silica, as claimed in claim 1, in a thixotropic paint or lacquer in order to get a thixotropic paint or lacquer having a viscosity reduced by less than 35% and a matting efficiency of less than 20 gloss units at an incidence angle of 60° and a loading of 5% by weight.

10

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/EP 93/03093A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C01B33/193 C09C1/30 C09D167/00 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C01B C09C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 442 325 (GRACE GMBH) 21 August 1991 cited in the application ---	
A	EP,A,0 341 383 (DEGUSSA AG) 15 November 1989 see claim 2 ---	2,4
A	US,A,4 127 641 (D.ALDCROFT ET AL.) 28 November 1978 see column 8, line 4 - line 30; example 6; table 1 *Table 1:Experiment 12* see claims 1-5,8 --- -/--	2,3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Intern nal Application No
PCT/EP 93/03093

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 94, no. 6, 9 February 1981, Columbus, Ohio, US; abstract no. 33070s, page 144 ; see abstract & JP,A,80 113 611 (TOKUYAMA SODA CO.,LTD.) 2 September 1980 ---	-
A	CHEMICAL ABSTRACTS, vol. 94, no. 6, 9 February 1981, Columbus, Ohio, US; abstract no. 33064t, page 144 ; see abstract & JP,A,80 116 613 (TOKUYAMA SODA CO.,LTD.) 8 September 1980 ---	
A	CHEMICAL ABSTRACTS, vol. 94, no. 6, 9 February 1981, Columbus, Ohio, US; abstract no. 33068x, page 144 ; see abstract & JP,A,80 116 614 (TOKUYAMA SODA CO.,LTD.) 8 September 1980 -----	

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 93/03093

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0442325	21-08-91	DE-C- 4004468	22-08-91
		DE-A- 4032619	16-04-92
		AU-B- 638544	01-07-93
		AU-A- 7093691	15-08-91
		US-A- 5221337	22-06-93
EP-A-0341383	15-11-89	DE-A- 3815670	25-01-90
		JP-A- 1320215	26-12-89
		JP-B- 5005767	25-01-93
		US-A- 5034207	23-07-91
		US-A- 5123964	23-06-92
US-A-4127641	28-11-78	NONE	
JP-A-80113611		NONE	
JP-A-80116613		NONE	
JP-A-80116614		NONE	